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(54) ZINC OXIDE MICROPARTICLE FOR ULTRAVIOLET SCREENING

(57)Abstract:

PROBLEM TO BE SOLVED: To provide zinc oxide microparticles excellent in dispersibility and ultraviolet screening effect.

SOLUTION: The zinc oxide microparticles for ultraviolet screening excellent in dispersibility has the following characteristics: the average primary particle size calculated based on specific surface area is $\leq 0.03 \mu\text{m}$, 0.1-20 mass%, based on zinc oxide, of at least one kind of Al or Si oxide or hydroxide is also contained inside the microparticles, and the bulk density is $\leq 0.25 \text{ g/ml}$.

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CLAIMS

[Claim(s)]

[Claim 1] The primary [an average of] particle diameter calculated from specific surface area is the zinc-oxide particle which is 0.03 micrometers or less, and it is aluminum also to the interior of the particle concerned. Or zinc-oxide particle for ultraviolet-rays electric shielding excellent in the dispersibility which contains one sort of the oxide of Si, or a hydroxide, or two sorts or more 0.1 to 20% with a mass ratio to a zinc oxide, and is characterized by bulk density being 0.25g/ml or less and which consists of a zinc oxide substantially.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the zinc-oxide particle for ultraviolet-rays electric shielding excellent in dispersibility, and relates to the zinc-oxide particle whose dispersibility improved notably in detail.

[0002]

[Description of the Prior Art] Although the zinc oxide was known as an ingredient which covers ultraviolet rays conventionally While the adverse effect beyond the anticipation which the environmental problem of the ultraviolet-rays trouble accompanying ozone hole amplification or ozone layer depletion comes to be greatly taken up by media etc. in recent years, and ultraviolet rays exert on the body becomes clear It is expected as one of the most typical ingredients for protecting the body from harmful ultraviolet rays, and research is done energetically and it is used for a wide range application. And the sunscreen cosmetics which blended the zinc oxide as an ultraviolet-rays electric shielding agent attract attention as a thing for coping with the adverse effect to such the body (skin).

[0003] Thus, in order not to block an operation of the natural makeup result of cosmetics original whose blended particle is a wrap **** product about the female skin simultaneously as well as the electric shielding function of harmful ultraviolet rays be excellent as the application which blends a zinc-oxide particle with cosmetics increases in recent years, to the visible ray, to be the most transparent possible ingredient came to be desired strongly. It is indispensable to follow, therefore to very-fine-particle-ize a zinc oxide more, and to make it transparence substantially to a visible ray.

[0004] the width which includes a near ultraviolet ray since a deer is carried out and the zinc-oxide system ultraviolet-rays electric shielding agents which are inorganic system compounds are absorbed and scattered about also in a near ultraviolet ray – it crosses to a large field and there is the advantage of cover ultraviolet rays , and since a zinc oxide is an inorganic compound , it is hard to cause allergy to the skin , and it becomes possible to blend so much into cosmetics . Therefore, it is blended especially with sunscreen cosmetics and effectiveness is demonstrated to the maximum extent.

[0005] And if the particle diameter is adjusted to an ultrafine particle 0.03 micrometers or less, since a zinc oxide will become much smaller than the wavelength of a visible ray, theoretically, most visible rays will not be absorbed, therefore the feeling of transparence of cosmetics will not be checked.

[0006] Thus, you may say that the zinc oxide which it atomized is what has the more excellent description compared with titanium oxide, the conventional ultraviolet-rays shielding material, i.e., organic ultraviolet ray absorbent, in respect of safety, the durability of an ultraviolet-rays shielding effect, etc. to the size of an ultraviolet-rays electric shielding field, a feeling of transparence, and the skin.

[0007]

[Problem(s) to be Solved by the Invention] However, even if it was in the particle-like zinc oxide which has the such ***** description, when this was used as an ultraviolet-rays electric shielding agent, this invention persons found out that there was a trouble described below.

[0008] That is, although a zinc-oxide particle has strong cohesive force from the first, when it atomizes as mentioned above, since the specific surface area is large, the cohesive force is also very big. And since cohesive force condenses a zinc-oxide particle by itself strongly the place which mixes with the basis of other organic systems and is usually used as mentioned above in blending such a zinc-oxide particle with the charge of makeup etc., the particle is not fully distributed in the organic system basis concerned. That is, the zinc-oxide particle condensed in this way had a possibility of checking the transparency of cosmetics original.

[0009] Moreover, when such a particle-like zinc oxide was blended with cosmetics, since these were condensing strongly, the delicate smoothness which the charge of makeup originally has was reduced, and there was a big problem of causing aggravation of a feel (touch).

[0010] The place which it was made in order that this invention might solve the above-mentioned trouble, and is made into the object is to offer the zinc oxide suitable for obtaining the charge of makeup in which it has good transparency, and an ultraviolet-rays shielding effect is high and shelf life moreover has good sufficient smoothness.

[0011]

[Means for Solving the Problem] Namely, if this invention is followed, it will be the zinc-oxide particle whose primary [an average of] particle diameter calculated from specific surface area is 0.03 micrometers or less. Also to the interior of the particle concerned, it is aluminum. Or one sort of the oxide of Si, or a hydroxide, or two sorts or more The zinc-oxide particle for ultraviolet-rays electric shielding excellent in the dispersibility which contains 0.1 to 20% with a mass ratio to a zinc oxide, and is characterized by bulk density being 0.25g/ml or less and which consists of a zinc oxide substantially is offered.

[0012]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail. 0.03 micrometers or less atomize the primary [an average of] particle diameter by which the zinc-oxide particle of this invention was calculated from specific surface area.

[0013] The primary [an average of] particle diameter calculated from specific surface area here is the value which measured specific surface area with the so-called BET adsorption method, calculated the acquired value by the degree type (1), and was acquired.

$d=1.06/S$ (1)

[d:primary [an average of] particle diameter in a formula (unit μm) and S:specific surface area (unit m^2/g)]

[0014] When the primary [an average of] particle diameter of a zinc-oxide particle exceeds 0.03 micrometers, the transparency of a visible ray is checked fundamentally and it is not desirable.

[0015] The zinc-oxide particle in this invention is aluminum further to the interior of the particle concerned while being very-fine-particle-ized in this way. Or it is characterized by having one sort or two sorts 0.1 to 20% with the mass ratio to a zinc oxide among the oxide of Si, or a hydroxide.

[0016] The oxide or hydroxide (the oxide of aluminum etc. may be called hereafter) of aluminum or Si in this invention has the function which raises the dispersibility of a zinc-oxide particle. A deer is carried out, it is important and, as for the oxide of these aluminum etc., it is [being introduced not only into the front face of a zinc-oxide particle but into the interior of a particle] inadequate to just be covered or covered by the particle front face. It is because in using the (i) zinc oxide for the reason it impresses a share (shearing force) by the agitator, a kneader, etc., a medium is made to distribute it, but a share quite strong against a particle starts inevitably, so the oxide of only aluminum which has only covered the particle front face etc. exfoliates from a particle easily in the distribution concerned. (ii) Since a new front face is exposed that floc and a welding particle can be broken etc., and this new particle front face has high activity and the oxide of aluminum etc. does not exist again when a share starts, re-condensation will be easily caused after distribution. Like the above, the dispersion effect cannot fully demonstrate only the zinc-oxide particle front face before distribution by what was covered with the oxide of aluminum etc.

[0017] In this invention, since improvement matter in dispersibility, such as an oxide of aluminum, is introduced also into the interior of a zinc-oxide particle, also when there is no problem of the above exfoliations and a particle breaks, the oxide of aluminum etc. exists in a new exposed surface, re-condensation is also prevented, and what was always distributed stably is obtained.

[0018] In this invention, although its one sort or two sorts or more contain aluminum etc. with the gestalt of an oxide or a hydroxide, the content is 0.1 - 10% preferably 0.1 to 20% in a mass ratio to a zinc oxide as the oxide or hydroxide of aluminum or Si. At less than 0.1%, the improvement effectiveness in dispersibility is not fully acquired, and since the effectiveness does not become still larger and the effective dose of a zinc oxide decreases conversely even if an addition is not much excessive and it adds exceeding 20%, the ultraviolet-rays shielding effect of zinc-oxide original will fall, and there are not much few contents of the oxide of aluminum etc., and it is not desirable. In addition, this content is the value calculated as that total quantity,

when using aluminum and Si together.

[0019] The bulk density of the zinc-oxide particle of this invention is 0.25g/ml or less again. Bulk density is JIS here. Although it is the value measured based on K5101, that this value is a value very low in ml and 0.25g/or less means that that space pulse duty factor is dramatically as small as only 4.4% or less, if the true density (5.6) of a zinc oxide is taken into consideration. That is, if micro level considers the zinc oxide very fine particle of this invention, it means occupying space in the very **** condition, and can be said to be existing in the scattering condition all over space so to speak. For this reason, the zinc-oxide particle of this invention is characterized by being in the condition which is very easy to distribute.

[0020] Furthermore, the particle of this invention is specified by being a zinc oxide substantially. The main peak according that it is a zinc oxide substantially to the X diffraction of the powder may show things that what is necessary is just the thing of a zinc oxide, and may contain the impurity mixed at the time of composition other than a zinc oxide, the impurity contained in a raw material.

[0021] Although the zinc-oxide particle of this invention is extremely excellent in the dispersibility, the measuring method shown below is used as the assessment approach of dispersibility.

[0022] 1. Weigh 1.5g of zinc oxides of a sample precisely, in addition to 50g of hexametaphosphoric acid sodium solutions, carry out distribution 10%PVA / 0.2% for 10 minutes (x15000rpm) with a homogenizer (the NIPPON SEIKI factory company make, ace homogenizer AM-7 mold), and obtain the dispersion liquid of a zinc-oxide particle.

[0023] 2. Set a 50-micrometer applicator on an auto applicator (the Imoto factory company make), and set a PET film (100 micrometers in thickness). The dispersion liquid of the above-mentioned zinc-oxide particle of optimum dose are carried on the PET film concerned, an auto applicator is switched on, and spreading is started. A feed rate is set as a graduation 20. A switch will be turned off if dispersion liquid are applied to the edge of a film in this way.

[0024] 3. Measure the thickness by the micrometer after drying a paint film for one day. Membranous thickness (about 5-10 micrometers) has gathered, a fixed part is started, a test piece is stuck on the part containing the incident light of the integrating sphere in a spectroscope (the Jasco Corp. make, V-570 ST mold), and permeability is measured.

[0025] Like the above, in the permeability which were measured by carrying out, light permeability is high and the thing which has low ultraviolet radiation permeability shows that the zinc-oxide particle is distributed finely.

[0026] The zinc-oxide particle of this invention has like the above the very good dispersibility of the particle which are evaluated by carrying out. Although the mechanism of this improvement in dispersibility now is not completely clear, this invention persons have guessed that it will probably be as follows once. That is, it is aluminum to a zinc-oxide particle. Or while the particle front face concerned serves as inactive and coherent [of particles] decreases by containing the oxide or hydroxide of Si, it is guessed that it is for compatibility with a medium to improve.

[0027] Especially as the manufacture approach of the zinc oxide concerning this invention, although it does not limit, the following approaches are adopted, for example. That is, in case the choke damp is blown into the water slurry containing a zinc oxide and basic zinc carbonate is compounded, the method of manufacturing a zinc oxide is desirable by adding a water-dispersion aluminum hydroxide, an aluminum oxide or a water-dispersion silicon hydroxide, and a silicon oxide, and decomposing the obtained basic zinc carbonate slurry concerned thermally, fluidized bed drying, medium fluidized bed drying, *****, or after carrying out spray drying.

[0028] As a zinc oxide used as a raw material, as long as it is the so-called zinc oxide, you may be what kind of thing. for example, the United States which oxidizes [which oxidizes and corks/ temporary quenching and /-returns] in zinc melting, the French method which is evaporated and oxidizes by the gaseous phase, and a zinc ore -- law -- Although things manufactured by any, such as a wet method (the decomposing method) which soda ash is added to a zinc salt solution, and basic zinc carbonate is settled, and is dried and calcinated, may be used, in order to obtain the zinc-oxide particle of a high grade, it is desirable to use a zinc oxide with

high purity.

[0029] Especially as water which is made to suspend this raw material zinc oxide, and is made into a slurry, it may not limit and any of the water supply system water except impurity particles, such as iron rust, the pure water which carried out the ion exchange, or distilled water may be used according to the demand purity of the zinc oxide which is a product. Moreover, although the choke damp to introduce may be used as it is as pure gas, it is also possible to use it for suitable concentration depending on the case, diluting with dilution gas, such as air and nitrogen.

[0030] As equipment for performing a basic zinc carbonate generation reaction Although it does not limit especially, for example A churning means, a heating means, gas installation / distribution means, And have introductory means, such as an oxide of aluminum, make it float, without settling a zinc-oxide particle, hold to a slurry regime, and the oxide of the choke damp and aluminum etc. is introduced into this. The reactor of the mixing vessel mold of the format which is made to contact a zinc-oxide particle and the choke damp enough under existence of particles, such as an oxide of aluminum, and can carry out a reaction is desirable.

[0031] as the slurry concentration of a raw material zinc oxide – at least 0.1 to 20 mass % – it is preferably desirable 0.1 to 10 mass % and to consider as the comparatively thin concentration of 1 - 5 mass % more preferably. When slurry concentration exceeds this range, the basic zinc carbonate of the diameter of a large drop generates, or it becomes difficult to consider as a particle with the sufficient dispersibility which floc becomes easy to generate and is made into the object by this invention. On the other hand, the amount of the water which should be removed in future desiccation processes etc. becomes excessive, when slurry concentration is not much thinner than this, manufacture effectiveness falls, and it is not desirable in energy.

[0032] As the introductory approach of the choke damp, if a slurry and gas can contact effectively, any approaches will be used. Although it does not limit especially, a perforated plate and the gas distribution machine (sparger) like a powder trachea are installed, for example in the reaction bottom of the tank section. Blow the choke damp into liquid through this sparger, and this is subdivided with an impeller still more preferably. How to decentralize and introduce into [whole] a slurry by making the choke damp into a minute air-bubbles group; as a reaction vessel, a well-closed container is used, the pressurized choke damp is introduced and means, such as an approach of making gas absorbing from the free surface of the slurry upper part, can be adopted. In the case of the latter, it is more desirable to form a vortex by churning, to perform compulsorily renewal of a front face of the slurry oil level concerned, and to promote gas absorption.

[0033] In case a carbon dioxide is blown and basic zinc carbonate is made to generate, the raw material of the oxide concerned or a hydroxide is added, and it is made to contain in basic zinc carbonate so that it may have one sort or two sorts 0.1 to 10% preferably 0.1 to 20% with a mass ratio to the zinc oxide concerned among the oxide of aluminum or Si, or a hydroxide. As a raw material, especially, as a desirable example, very fine particle sols, such as colloidal silica and a colloidal alumina, are mentioned, and these are introduced into reaction mixture with the introductory means like dropping equipment. In addition, as long as it, in addition to this, produces the oxide or hydroxide of aluminum and Si by blowing the choke damp, what kind of compound may be used. As for these colloidal silica etc., it is desirable to introduce almost continuously with means, such as dropping, according to the speed of supply of the choke damp. Since detailed sol particles, such as an oxide of aluminum, always exist in near where the particle of basic zinc carbonate generates and grows in this way, the particle growth concerned is performed so that very fine particles, such as an oxide of aluminum, may be incorporated, and it is thought that the oxide of aluminum etc. will exist in the interior of the basic zinc carbonate particle formed in this way.

[0034] as a churning means – both the usual agitator, for example, a paddle agitator, a propeller mold agitator a turbine mold agitator, etc. – although – it is used suitably.

[0035] Although the basic zinc carbonate generation reaction of this invention can be actually carried out with various methods For example, the zinc-oxide slurry is first taught to the reaction vessel. The half-continuous magnetization method which the choke damp is continuously supplied [continuous magnetization method] to this and makes a basic zinc carbonate slurry generate (half-batch process); Supply both zinc-oxide slurry and

choke damp to a reaction vessel continuously, and a basic zinc carbonate slurry is made to generate. Approaches, such as a continuous magnetization method which carries out carrying out overflow etc. and extracts the generated basic zinc carbonate slurry concerned from a reaction vessel continuously, are adopted preferably.

[0036] Especially as reaction temperature of a basic zinc carbonate generation reaction, although it does not limit, 10-80 degrees C is 20-60 degrees C preferably. Although the reaction itself advances at high speed so that temperature is high, the solubility to the water of the choke damp will decrease, if temperature becomes high, and the gas concentration in liquid falls. Therefore, reaction temperature is even if lower than the above-mentioned temperature requirement, Even if high, an all-inclusive reaction rate becomes late and is not desirable. Moreover, although reaction time (mean flow-time [in / in the case of a continuous magnetization method / a reaction vessel]) may change with reaction temperature, the carbon dioxide levels introduced, it is usually 30 minutes - about 5 hours preferably for 10 minutes to 10 hours. In addition, as for a reactor, it is also desirable to have a heating means, an incubation means, and a temperature control means because of temperature maintenance.

[0037] In this invention, the slurry containing the basic zinc carbonate obtained by the above basic zinc carbonate generation reaction is dried by fluidized bed drying, medium fluidized bed drying, *****, or spray drying, moisture is removed, and it considers as desiccation powder.

[0038] In this case, since the slurry concentration of the slurry containing basic zinc carbonate is quite low, it is not desirable on heat energy economy. [of drying this as it is] Therefore, it is desirable preferably to condense the slurry concerned by concentration, especially the mechanical means beforehand.

[0039] although the concentration slurry concerned holds a fluidity and it atomizes to a fluidized bed dryer etc., and there will be especially no limit about the enrichment of a slurry if it is supply and the range processed – general – as slurry concentration – 20 to 50 mass % – it is preferably desirable from the point of a handling top and profitability 20 to 45 mass % and that it is the range of 25 - 40 mass % still more preferably.

[0040] Especially as a mechanical means for concentration, although it does not limit, the centrifugal classification using the centrifugation and the liquid cyclone using the precipitate concentration and the centrifugal settler using a thickener etc. is used preferably, and can adopt the optimal equipment according to desired enrichment, a desired throughput, etc.

[0041] In this invention, like the above, a basic zinc carbonate slurry is condensed beforehand preferably, and a fluidized bed dryer, a medium fluidized bed dryer, *****, or a spray dryer solves it, and it is supplied and dried by the dryer. It dries extremely for a short time, drying, this forming the fluid bed by the hot blast for desiccation, and floating, or (fluidized bed drying, medium fluidized bed drying) being conveyed [become the drop in which the supplied slurry contains a very fine particle within this dryer,] by hot blast (***** or spray drying), and the desiccation powder of basic zinc carbonate is obtained.

[0042] Especially a spray dryer is desirable at the point that the desiccation particle of the basic zinc carbonate distributed most is obtained as a dryer. As a sprayer in the case of using a spray dryer, it is desirable that a rotating disk, a two fluid nozzle, a pressure nozzle, etc. can adopt suitably, and make hot blast temperature for desiccation into 200-300 degrees C at the entrance, and it makes it about 100-150 degrees C at an outlet.

[0043] Finally the dried basic zinc carbonate concerned is decomposed thermally (baking), and it considers as a zinc oxide. Thermal decomposition temperature is the temperature which disassembles basic zinc carbonate into the zinc oxide of the shape of a particle with sufficient dispersibility, and is still more preferably desirable 200-500 degrees C preferably 200-1000 degrees C. [of the temperature of 250-350 degrees C] Since decomposition will become imperfection if temperature is not much lower than this, and dispersibility will all worsen [that a particle grows too much by condensation or sintering, and] if temperature is too higher not much than this, it is not desirable. Whenever [throughput and stoving temperature], although thermal decomposition time amount may change with molds of a heating furnace etc., it is usually about 1 - 10 hours preferably for 30 minutes to 20 hours.

[0044] Thermal decomposition is performed under oxidizing atmospheres, such as air, by the furnace which

can heat a basic zinc carbonate particle to the above-mentioned temperature. Especially as a heating furnace, it does not limit and a box furnace, a rotary furnace (rotary kiln), a moving-bed furnace, a fluid bed furnace, an electric furnace, a gas heating furnace, an infrared heating furnace, etc. are used suitably.

[0045] The zinc-oxide grain particle after thermal decomposition is excellent in dispersibility, and applicable to ultraviolet-rays electric shielding, such as cosmetics of this invention, as it is. In addition, by request, after carrying out grinding processing further with pulverizers, such as a ball mill, a rod mill, an attrition mill, a jet mill, and a micron mill, it can also be used. These pulverizers are suitably chosen according to cosmetics, etc. a coating, etc. to blend.

[0046]

[Example] Hereafter, an example explains this invention. However, these are examples of the mode of mere operation and the technical range of this invention is not limited at all by these.

[0047] (Example 1)

(1) JIS obtained with the French method K1410 The zinc-oxide slurry of 62.5 g/L was prepared using an one-sort zinc oxide and ion exchange water. The pars basilaris ossis occipitalis of content volume 10L was equipped with the powder trachea for this slurry, it 5.6L Taught the reaction container which the agitator, the slurry supply means, and the incubation device attached, temperature was kept at 30 degrees C, and the choke damp was blown into the bottom of churning by part for 5L/. While blowing this gas, dropping supply of the colloidal silica solution (concentration 12.5g-SiO₂/L) 1.4L was continuously carried out over 2 hours. It checked that ended an entrainment 2 hours after, carried out XRD analysis of the product, and basic zinc carbonate was generating.

[0048] (2) After putting this slurry for 2 hours, supernatant liquor was thrown away and the basic zinc carbonate slurry of 20% of slurry concentration was obtained. It checked that supernatant liquor was analyzed and the amount of silica was not. That is, it was checked that parts for all the supplied silica had been introduced into basic zinc carbonate. Feed of this slurry was carried out to the spray dryer adjusted to the inlet gas temperature of 250 degrees C, and the outlet gas temperature of 130 degrees C, and the basic zinc carbonate particle was obtained. The particle diameter of this particle was about 100 micrometers.

[0049] (3) It inserted in the core box fumace which heated this particle at 250 degrees C, and decomposed thermally for 5 hours, and the zinc-oxide very fine particle was obtained.

[0050] The specific surface area of the obtained zinc oxide was measured with the BET adsorption method, and the value of 50m²/g was acquired. The particle diameter calculated from this specific surface area is 0.02 micrometers. Moreover, it checked that analyzed a part for the silica in a zinc oxide, and a part for 4.8% of silica was included. JIS The bulk density measured based on K5101 was 0.20g/ml.

[0051] Next, in order to evaluate the dispersibility of this obtained zinc-oxide very fine particle, the above-mentioned dispersibility assessment trial was performed and permeability was measured. A result is shown in a table 1. It turns out that the zinc oxide of this invention excels [ability / light permeability and / ultraviolet-rays electric shielding] in dispersibility highly so that clearly from a table.

[0052] (Example 1 of a comparison)

(1) The zinc-oxide slurry of 50 g/L was prepared using the JIS K1401 one-sort zinc oxide and ion exchange water which were obtained with the French method. This slurry was 7L Taught to the reaction container which equipped the agitator and pars basilaris ossis occipitalis of content volume 10L with the powder trachea, and the choke damp was blown by part for bottom of churning 5L/. It checked that carried out XRD analysis of the entrainment 2 hours after, and basic zinc carbonate was generating the stop and the product.

[0053] (2) After putting this slurry for 2 hours, except for supematant liquor, the basic zinc carbonate slurry of 20% of slurry concentration was obtained. Feed of this slurry was carried out to the spray dryer adjusted to the inlet gas temperature of 250 degrees C, and the outlet gas temperature of 130 degrees C, and the basic zinc carbonate particle was obtained. The particle diameter of this particle was about 110 micrometers.

[0054] (3) It inserted in the core box fumace which heated this particle at 250 degrees C, and decomposed thermally for 5 hours, and the zinc-oxide very fine particle was obtained.

[0055] The specific surface area of the obtained zinc oxide was measured with the BET adsorption method, and the value of 47m²/g was acquired. The particle diameter calculated from this specific surface area is 0.02 micrometers. The bulk density measured based on JIS K5101 was 0.30g/ml. Next, in order to measure the dispersibility of this obtained zinc-oxide very fine particle, the above-mentioned dispersibility assessment trial was performed and permeability was measured. A result is shown in the following table 1. Although the zinc oxide manufactured using the conventional approach contains neither aluminum nor the oxide of Si, and light permeability is high compared with an example 1 since bulk density is also high, ultraviolet-rays electric shielding ability is low, and it turns out that it is inferior to dispersibility so that clearly from a table.

[0056] (Example 2 of a comparison) Using the zinc oxide obtained in the example 1 of a comparison, in addition to the sodium-silicate water solution of computational complexity with which the amount of silica coats becomes 5 mass %, after agitating this solution strongly and making it a slurry regime, the hydrochloric acid was added gradually and the lowering silicon oxide was deposited to pH7. The zinc-oxide powder which filtration[after 1 evening standing]-washed this liquid, dried, and covered the front face with the silicon oxide was obtained. The dispersibility assessment trial of this zinc-oxide powder was performed, and permeability was measured. A result is shown in the following table 1. Although the light permeability of what covered only the front face of a zinc oxide with the silica is high compared with an example 1 as shown in a table, ultraviolet-rays electric shielding ability is low, and it turns out that it is inferior to dispersibility.

[0057] (Example 2)

(1) The zinc-oxide slurry of 50 g/L was prepared using the supernatant liquor and pure water which were obtained in the JIS K1410 three-sort zinc oxide obtained with the French method, and the example 1. This slurry was 5.6L Taught to the reaction container which equipped the pars basilaris ossis occipitalis of content volume 10L with the powder trachea, and the agitator, the slurry supply means, and the incubation device attached, temperature was kept at 40 degrees C, and the choke damp was blown by part for bottom of churning 10L/. Colloidal alumina while blowing this gas solution (concentration 12.5 g-aluminum₂O₃/L) 1.4L was continuously supplied over 2 hours. It checked that ended an entrainment 2 hours after, carried out XRD analysis of the product, and basic zinc carbonate was generating.

[0058] (2) After putting this slurry for 2 hours, supernatant liquor was thrown away and the basic zinc carbonate slurry of 27% of slurry concentration was obtained. Feed of this slurry was carried out to the spray dryer adjusted to the inlet gas temperature of 250 degrees C, and the outlet gas temperature of 130 degrees C, and the basic zinc carbonate particle was obtained. The particle diameter of this particle was about 400 micrometers.

[0059] (3) It inserted in the retort furnace (the retort was rotated by 10rpm) which heated the particle concerned at 300 degrees C, and decomposed thermally for 5 hours, and the zinc-oxide very fine particle was obtained. The specific surface area of the obtained zinc oxide was measured with the BET adsorption method, and the value of 43m²/g was acquired. The particle diameter calculated from this specific surface area is 0.02 micrometers. Moreover, it checked that analyzed a part for the alumina in a zinc oxide, and 0.9% of alumina was included. JIS The bulk density measured based on K5105 was 0.3g/ml.

[0060] Next, in order to evaluate the dispersibility of this obtained zinc-oxide very fine particle, the above-mentioned dispersibility assessment trial was performed and permeability was measured. A result is shown in the following table 1. It turns out that the zinc oxide of this invention excels [ability / light permeability and / ultraviolet-rays electric shielding] in dispersibility highly so that clearly from a table.

[0061] (Example 3)

(1) The zinc-oxide slurry of 62.5 g/L was prepared using the JIS K1410 one-sort zinc oxide and ion exchange water which were obtained with the French method. This slurry was 5.6L Taught to the reaction container which equipped the pars basilaris ossis occipitalis of content volume 10L with the powder trachea, and the agitator, the slurry supply means, and the incubation device attached, temperature was kept at 30 degrees C, and the choke damp was blown by part for bottom of churning 5L/. While blowing this gas, colloidal silica solution (concentration 25g-SiO₂/L) 1.4L was continuously supplied over 2 hours. It checked that ended an

entrainment 2 hours after, carried out XRD analysis of the product, and basic zinc carbonate was generating.

[0062] (2) After putting this slurry for 2 hours, supernatant liquor was thrown away and the basic zinc carbonate slurry of 20% of slurry concentration was obtained. It checked that supernatant liquor was analyzed and the amount of silica was not. Feed of this slurry was carried out to the spray dryer adjusted to the inlet gas temperature of 250 degrees C, and the outlet gas temperature of 130 degrees C, and the basic zinc carbonate particle was obtained. The particle diameter of this particle was about 100 micrometers.

[0063] (3) It inserted in the core box furnace which heated this particle at 250 degrees C, and decomposed thermally for 5 hours, and the zinc-oxide very fine particle was obtained. The specific surface area of the obtained zinc oxide was measured with the BET adsorption method, and the value of 55m²/g was acquired. The particle diameter calculated from this specific surface area is 0.02 micrometers. Moreover, it checked that analyzed a part for the silica in a zinc oxide, and a part for 9% of silica was included. JIS The bulk density measured based on K5105 was 0.20g/ml.

[0064] Next, in order to measure the dispersibility of this obtained zinc-oxide very fine particle, the above-mentioned dispersibility assessment trial was performed and permeability was measured. A result is shown in the following table 1. It turns out that the zinc oxide of this invention excels [ability / light permeability and / ultraviolet-rays electric shielding] in dispersibility highly so that clearly from a table.

[0065]

[A table 1]

[0066]

	透過率 (%)	
	550nm	350nm
実施例 1	96.65	26.32
実施例 2	96.92	28.35
実施例 3	97.65	31.63
比較例 1	95.31	34.40
比較例 2	96.46	41.56

[Effect of the Invention] It turns out that it is the zinc-oxide particle for ultraviolet-rays electric shielding which the zinc-oxide particle of this invention excels [ability / light permeability and / ultraviolet-rays electric shielding] in dispersibility highly so that clearly from a table, and was excellent in dispersibility. Therefore, it is used for ultraviolet-rays electric shielding and coincidence, such as cosmetics and a coating, suitable for the various applications which need transparency.

TECHNICAL FIELD

[Field of the Invention] This invention relates to the zinc-oxide particle for ultraviolet-rays electric shielding excellent in dispersibility, and relates to the zinc-oxide particle whose dispersibility improved notably in detail.

PRIOR ART

[Description of the Prior Art] Although the zinc oxide was known as an ingredient which covers ultraviolet rays conventionally While the adverse effect beyond the anticipation which the environmental problem of the ultraviolet-rays trouble accompanying ozone hole amplification or ozone layer depletion comes to be greatly taken up by media etc. in recent years, and ultraviolet rays exert on the body becomes clear It is expected as

one of the most typical ingredients for protecting the body from harmful ultraviolet rays, and research is done energetically and it is used for a wide range application. And the sunscreen cosmetics which blended the zinc oxide as an ultraviolet-rays electric shielding agent attract attention as a thing for coping with the adverse effect to such the body (skin).

[0003] Thus, in order not to block an operation of the natural makeup result of cosmetics original whose blended particle is a wrap **** product about the female skin simultaneously as well as the electric shielding function of harmful ultraviolet rays be excellent as the application which blends a zinc-oxide particle with cosmetics increases in recent years, to the visible ray, to be the most transparent possible ingredient came to be desired strongly. It is indispensable to follow, therefore to very-fine-particle-ize a zinc oxide more, and to make it transparence substantially to a visible ray.

[0004] the width which includes a near ultraviolet ray since a deer is carried out and the zinc-oxide system ultraviolet-rays electric shielding agents which are inorganic system compounds are absorbed and scattered about also in a near ultraviolet ray – it crosses to a large field and there is the advantage of cover ultraviolet rays , and since a zinc oxide is an inorganic compound , it is hard to cause allergy to the skin , and it becomes possible to blend so much into cosmetics . Therefore, it is blended especially with sunscreen cosmetics and effectiveness is demonstrated to the maximum extent.

[0005] And if the particle diameter is adjusted to an ultrafine particle 0.03 micrometers or less, since a zinc oxide will become much smaller than the wavelength of a visible ray, theoretically, most visible rays will not be absorbed, therefore the feeling of transparence of cosmetics will not be checked.

[0006] Thus, you may say that the zinc oxide which it atomized is what has the more excellent description compared with titanium oxide, the conventional ultraviolet-rays shielding material, i.e., organic ultraviolet ray absorbent, in respect of safety, the durability of an ultraviolet-rays shielding effect, etc. to the size of an ultraviolet-rays electric shielding field, a feeling of transparence, and the skin.

EFFECT OF THE INVENTION

[Effect of the Invention] It turns out that it is the zinc-oxide particle for ultraviolet-rays electric shielding which the zinc-oxide particle of this invention excels [ability / light permeability and / ultraviolet-rays electric shielding] in dispersibility highly so that clearly from a table, and was excellent in dispersibility. Therefore, it is used for ultraviolet-rays electric shielding and coincidence, such as cosmetics and a coating, suitable for the various applications which need transparency.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] However, even if it was in the particle-like zinc oxide which has the such ***** description, when this was used as an ultraviolet-rays electric shielding agent, this invention persons found out that there was a trouble described below.

[0008] That is, although a zinc-oxide particle has strong cohesive force from the first, when it atomizes as mentioned above, since the specific surface area is large, the cohesive force is also very big. And since cohesive force condenses a zinc-oxide particle by itself strongly the place which mixes with the basis of other organic systems and is usually used as mentioned above in blending such a zinc-oxide particle with the charge of makeup etc., the particle is not fully distributed in the organic system basis concerned. That is, the zinc-oxide particle condensed in this way had a possibility of checking the transparency of cosmetics original.

[0009] Moreover, when such a particle-like zinc oxide was blended with cosmetics, since these were condensing strongly, the delicate smoothness which the charge of makeup originally has was reduced, and there was a big problem of causing aggravation of a feel (touch).

[0010] The place which it was made in order that this invention might solve the above-mentioned trouble, and is made into the object is to offer the zinc oxide suitable for obtaining the charge of makeup in which it has good transparency, and an ultraviolet-rays shielding effect is high and shelf life moreover has good sufficient smoothness.

MEANS

[Means for Solving the Problem] Namely, if this invention is followed, it will be the zinc-oxide particle whose primary [an average of] particle diameter calculated from specific surface area is 0.03 micrometers or less. Also to the interior of the particle concerned, it is aluminum. Or one sort of the oxide of Si, or a hydroxide, or two sorts or more The zinc-oxide particle for ultraviolet-rays electric shielding excellent in the dispersibility which contains 0.1 to 20% with a mass ratio to a zinc oxide, and is characterized by bulk density being 0.25g/ml or less and which consists of a zinc oxide substantially is offered.

[0012]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail. 0.03 micrometers or less atomize the primary [an average of] particle diameter by which the zinc-oxide particle of this invention was calculated from specific surface area.

[0013] The primary [an average of] particle diameter calculated from specific surface area here is the value which measured specific surface area with the so-called BET adsorption method, calculated the acquired value by the degree type (1), and was acquired.

$d=1.06/S$ (1)

[d:primary [an average of] particle diameter in a formula (unit μm) and S:specific surface area (unit m^2/g)]

[0014] When the primary [an average of] particle diameter of a zinc-oxide particle exceeds 0.03 micrometers, the transparency of a visible ray is checked fundamentally and it is not desirable.

[0015] The zinc-oxide particle in this invention is aluminum further to the interior of the particle concerned while being very-fine-particle-ized in this way. Or it is characterized by having one sort or two sorts 0.1 to 20% with the mass ratio to a zinc oxide among the oxide of Si, or a hydroxide.

[0016] The oxide or hydroxide (the oxide of aluminum etc. may be called hereafter) of aluminum or Si in this invention has the function which raises the dispersibility of a zinc-oxide particle. A deer is carried out, it is important and, as for the oxide of these aluminum etc., it is [being introduced not only into the front face of a zinc-oxide particle but into the interior of a particle] inadequate to just be covered or covered by the particle front face. It is because in using the (i) zinc oxide for the reason it impresses a share (shearing force) by the agitator, a kneader, etc., a medium is made to distribute it, but a share quite strong against a particle starts inevitably, so the oxide of only aluminum which has only covered the particle front face etc. exfoliates from a particle easily in the distribution concerned. (ii) Since a new front face is exposed that floc and a welding particle can be broken etc., and this new particle front face has high activity and the oxide of aluminum etc. does not exist again when a share starts, re-condensation will be easily caused after distribution. Like the above, the dispersion effect cannot fully demonstrate only the zinc-oxide particle front face before distribution by what was covered with the oxide of aluminum etc.

[0017] In this invention, since improvement matter in dispersibility, such as an oxide of aluminum, is introduced also into the interior of a zinc-oxide particle, also when there is no problem of the above exfoliations and a particle breaks, the oxide of aluminum etc. exists in a new exposed surface, re-condensation is also prevented, and what was always distributed stably is obtained.

[0018] In this invention, although its one sort or two sorts or more contain aluminum etc. with the gestalt of an oxide or a hydroxide, the content is 0.1 - 10% preferably 0.1 to 20% in a mass ratio to a zinc oxide as the oxide or hydroxide of aluminum or Si. At less than 0.1%, the improvement effectiveness in dispersibility is not fully acquired, and since the effectiveness does not become still larger and the effective dose of a zinc oxide

decreases conversely even if an addition is not much excessive and it adds exceeding 20%, the ultraviolet-rays shielding effect of zinc-oxide original will fall, and there are not much few contents of the oxide of aluminum etc., and it is not desirable. In addition, this content is the value calculated as that total quantity, when using aluminum and Si together.

[0019] The bulk density of the zinc-oxide particle of this invention is 0.25g/ml or less again. Bulk density is JIS here. Although it is the value measured based on K5101, that this value is a value very low in ml and 0.25g /or less means that that space pulse duty factor is dramatically as small as only 4.4% or less, if the true density (5.6) of a zinc oxide is taken into consideration. That is, if micro level considers the zinc oxide very fine particle of this invention, it means occupying space in the very **** condition, and can be said to be existing in the scattering condition all over space so to speak. For this reason, the zinc-oxide particle of this invention is characterized by being in the condition which is very easy to distribute.

[0020] Furthermore, the particle of this invention is specified by being a zinc oxide substantially. The main peak according that it is a zinc oxide substantially to the X diffraction of the powder may show things that what is necessary is just the thing of a zinc oxide, and may contain the impurity mixed at the time of composition other than a zinc oxide, the impurity contained in a raw material.

[0021] Although the zinc-oxide particle of this invention is extremely excellent in the dispersibility, the measuring method shown below is used as the assessment approach of dispersibility.

[0022] 1. Weigh 1.5g of zinc oxides of a sample precisely, in addition to 50g of hexametaphosphoric acid sodium solutions, carry out distribution 10%PVA / 0.2% for 10 minutes (x15000rpm) with a homogenizer (the NIPPON SEIKI factory company make, ace homogenizer AM-7 mold), and obtain the dispersion liquid of a zinc-oxide particle.

[0023] 2. Set a 50-micrometer applicator on an auto applicator (the Imoto factory company make), and set a PET film (100 micrometers in thickness). The dispersion liquid of the above-mentioned zinc-oxide particle of optimum dose are carried on the PET film concerned, an auto applicator is switched on, and spreading is started. A feed rate is set as a graduation 20. A switch will be turned off if dispersion liquid are applied to the edge of a film in this way.

[0024] 3. Measure the thickness by the micrometer after drying a paint film for one day. Membranous thickness (about 5-10 micrometers) has gathered, a fixed part is started, a test piece is stuck on the part containing the incident light of the integrating sphere in a spectroscopy (the Jasco Corp. make, V-570 ST mold), and permeability is measured.

[0025] Like the above, in the permeability which were measured by carrying out, light permeability is high and the thing which has low ultraviolet radiation permeability shows that the zinc-oxide particle is distributed finely.

[0026] The zinc-oxide particle of this invention has like the above the very good dispersibility of the particle which are evaluated by carrying out. Although the mechanism of this improvement in dispersibility now is not completely clear, this invention persons have guessed that it will probably be as follows once. That is, it is aluminum to a zinc-oxide particle. Or while the particle front face concerned serves as inactive and coherent [of particles] decreases by containing the oxide or hydroxide of Si, it is guessed that it is for compatibility with a medium to improve.

[0027] Especially as the manufacture approach of the zinc oxide concerning this invention, although it does not limit, the following approaches are adopted, for example. That is, in case the choke damp is blown into the water slurry containing a zinc oxide and basic zinc carbonate is compounded, the method of manufacturing a zinc oxide is desirable by adding a water-dispersion aluminum hydroxide, an aluminum oxide or a water-dispersion silicon hydroxide, and a silicon oxide, and decomposing the obtained basic zinc carbonate slurry concerned thermally, fluidized bed drying, medium fluidized bed drying, *****, or after carrying out spray drying.

[0028] As a zinc oxide used as a raw material, as long as it is the so-called zinc oxide, you may be what kind of thing. for example, the United States which oxidizes [which oxidizes and corks/ temporary quenching and /-returns] in zinc melting, the French method which is evaporated and oxidizes by the gaseous phase, and a

zinc ore – law – Although things manufactured by any, such as a wet method (the decomposing method) which soda ash is added to a zinc salt solution, and basic zinc carbonate is settled, and is dried and calcinated, may be used, in order to obtain the zinc-oxide particle of a high grade, it is desirable to use a zinc oxide with high purity.

[0029] Especially as water which is made to suspend this raw material zinc oxide, and is made into a slurry, it may not limit and any of the water supply system water except impurity particles, such as iron rust, the pure water which carried out the ion exchange, or distilled water may be used according to the demand purity of the zinc oxide which is a product. Moreover, although the choke damp to introduce may be used as it is as pure gas, it is also possible to use it for suitable concentration depending on the case, diluting with dilution gas, such as air and nitrogen.

[0030] As equipment for performing a basic zinc carbonate generation reaction Although it does not limit especially, for example A churning means, a heating means, gas installation / distribution means, And have introductory means, such as an oxide of aluminum, make it float, without settling a zinc-oxide particle, hold to a slurry regime, and the oxide of the choke damp and aluminum etc. is introduced into this. The reactor of the mixing vessel mold of the format which is made to contact a zinc-oxide particle and the choke damp enough under existence of particles, such as an oxide of aluminum, and can carry out a reaction is desirable.

[0031] as the slurry concentration of a raw material zinc oxide – at least 0.1 to 20 mass % – it is preferably desirable 0.1 to 10 mass % and to consider as the comparatively thin concentration of 1 - 5 mass % more preferably. When slurry concentration exceeds this range, the basic zinc carbonate of the diameter of a large drop generates, or it becomes difficult to consider as a particle with the sufficient dispersibility which floc becomes easy to generate and is made into the object by this invention. On the other hand, the amount of the water which should be removed in future desiccation processes etc. becomes excessive, when slurry concentration is not much thinner than this, manufacture effectiveness falls, and it is not desirable in energy.

[0032] As the introductory approach of the choke damp, if a slurry and gas can contact effectively, any approaches will be used. Although it does not limit especially, a perforated plate and the gas distribution machine (sparger) like a powder trachea are installed, for example in the reaction bottom of the tank section. Blow the choke damp into liquid through this sparger, and this is subdivided with an impeller still more preferably. How to decentralize and introduce into [whole] a slurry by making the choke damp into a minute air-bubbles group; as a reaction vessel, a well-closed container is used, the pressurized choke damp is introduced and means, such as an approach of making gas absorbing from the free surface of the slurry upper part, can be adopted. In the case of the latter, it is more desirable to form a vortex by churning, to perform compulsorily renewal of a front face of the slurry oil level concerned, and to promote gas absorption.

[0033] In case a carbon dioxide is blown and basic zinc carbonate is made to generate, the raw material of the oxide concerned or a hydroxide is added, and it is made to contain in basic zinc carbonate so that it may have one sort or two sorts 0.1 to 10% preferably 0.1 to 20% with a mass ratio to the zinc oxide concerned among the oxide of aluminum or Si, or a hydroxide. As a raw material, especially, as a desirable example, very fine particle sols, such as colloidal silica and a colloidal alumina, are mentioned, and these are introduced into reaction mixture with the introductory means like dropping equipment. In addition, as long as it, in addition to this, produces the oxide or hydroxide of aluminum and Si by blowing the choke damp, what kind of compound may be used. As for these colloidal silica etc., it is desirable to introduce almost continuously with means, such as dropping, according to the speed of supply of the choke damp. Since detailed sol particles, such as an oxide of aluminum, always exist in near where the particle of basic zinc carbonate generates and grows in this way, the particle growth concerned is performed so that very fine particles, such as an oxide of aluminum, may be incorporated, and it is thought that the oxide of aluminum etc. will exist in the interior of the basic zinc carbonate particle formed in this way.

[0034] as a churning means – both the usual agitator, for example, a paddle agitator, a propeller mold agitator a turbine mold agitator, etc. – although – it is used suitably.

[0035] Although the basic zinc carbonate generation reaction of this invention can be actually carried out with

various methods For example, the zinc-oxide slurry is first taught to the reaction vessel. The half-continuous magnetization method which the choke damp is continuously supplied [continuous magnetization method] to this and makes a basic zinc carbonate slurry generate (half-batch process); Supply both zinc-oxide slurry and choke damp to a reaction vessel continuously, and a basic zinc carbonate slurry is made to generate. Approaches, such as a continuous magnetization method which carries out carrying out overflow etc. and extracts the generated basic zinc carbonate slurry concerned from a reaction vessel continuously, are adopted preferably.

[0036] Especially as reaction temperature of a basic zinc carbonate generation reaction, although it does not limit, 10-80 degrees C is 20-60 degrees C preferably. Although the reaction itself advances at high speed so that temperature is high, the solubility to the water of the choke damp will decrease, if temperature becomes high, and the gas concentration in liquid falls. Therefore, reaction temperature is even if lower than the above-mentioned temperature requirement, Even if high, an all-inclusive reaction rate becomes late and is not desirable. Moreover, although reaction time (mean flow-time [in / in the case of a continuous magnetization method / a reaction vessel]) may change with reaction temperature, the carbon dioxide levels introduced, it is usually 30 minutes - about 5 hours preferably for 10 minutes to 10 hours. In addition, as for a reactor, it is also desirable to have a heating means, an incubation means, and a temperature control means because of temperature maintenance.

[0037] In this invention, the slurry containing the basic zinc carbonate obtained by the above basic zinc carbonate generation reaction is dried by fluidized bed drying, medium fluidized bed drying, *****, or spray drying, moisture is removed, and it considers as desiccation powder.

[0038] In this case, since the slurry concentration of the slurry containing basic zinc carbonate is quite low, it is not desirable on heat energy economy. [of drying this as it is] Therefore, it is desirable preferably to condense the slurry concerned by concentration, especially the mechanical means beforehand.

[0039] although the concentration slurry concerned holds a fluidity and it atomizes to a fluidized bed dryer etc., and there will be especially no limit about the enrichment of a slurry if it is supply and the range processed – general – as slurry concentration – 20 to 50 mass % – it is preferably desirable from the point of a handling top and profitability 20 to 45 mass % and that it is the range of 25 - 40 mass % still more preferably.

[0040] Especially as a mechanical means for concentration, although it does not limit, the centrifugal classification using the centrifugation and the liquid cyclone using the precipitate concentration and the centrifugal settler using a thickener etc. is used preferably, and can adopt the optimal equipment according to desired enrichment, a desired throughput, etc.

[0041] In this invention, like the above, a basic zinc carbonate slurry is condensed beforehand preferably, and a fluidized bed dryer, a medium fluidized bed dryer, *****, or a spray dryer solves it, and it is supplied and dried by the dryer. It dries extremely for a short time, drying, this forming the fluid bed by the hot blast for desiccation, and floating, or (fluidized bed drying, medium fluidized bed drying) being conveyed [become the drop in which the supplied slurry contains a very fine particle within this dryer,] by hot blast (***** or spray drying), and the desiccation powder of basic zinc carbonate is obtained.

[0042] Especially a spray dryer is desirable at the point that the desiccation particle of the basic zinc carbonate distributed most is obtained as a dryer. As a sprayer in the case of using a spray dryer, it is desirable that a rotating disk, a two fluid nozzle, a pressure nozzle, etc. can adopt suitably, and make hot blast temperature for desiccation into 200-300 degrees C at the entrance, and it makes it about 100-150 degrees C at an outlet.

[0043] Finally the dried basic zinc carbonate concerned is decomposed thermally (baking), and it considers as a zinc oxide. Thermal decomposition temperature is the temperature which disassembles basic zinc carbonate into the zinc oxide of the shape of a particle with sufficient dispersibility, and is still more preferably desirable 200-500 degrees C preferably 200-1000 degrees C. [of the temperature of 250-350 degrees C] Since decomposition will become imperfection if temperature is not much lower than this, and dispersibility will all worsen [that a particle grows too much by condensation or sintering, and] if temperature is too higher not much than this, it is not desirable. Whenever [throughput and stoving temperature], although thermal

decomposition time amount may change with molds of a heating furnace etc., it is usually about 1 - 10 hours preferably for 30 minutes to 20 hours.

[0044] Thermal decomposition is performed under oxidizing atmospheres, such as air, by the furnace which can heat a basic zinc carbonate particle to the above-mentioned temperature. Especially as a heating furnace, it does not limit and a box furnace, a rotary furnace (rotary kiln), a moving-bed furnace, a fluid bed furnace, an electric furnace, a gas heating furnace, an infrared heating furnace, etc. are used suitably.

[0045] The zinc-oxide grain particle after thermal decomposition is excellent in dispersibility, and applicable to ultraviolet-rays electric shielding, such as cosmetics of this invention, as it is. In addition, by request, after carrying out grinding processing further with pulverizers, such as a ball mill, a rod mill, an attrition mill, a jet mill, and a micron mill, it can also be used. These pulverizers are suitably chosen according to cosmetics, etc. a coating, etc. to blend.

EXAMPLE

[Example] Hereafter, an example explains this invention. However, these are examples of the mode of mere operation and the technical range of this invention is not limited at all by these.

[0047] (Example 1)

(1) JIS obtained with the French method K1410 The zinc-oxide slurry of 62.5 g/L was prepared using an one-sort zinc oxide and ion exchange water. The pars basilaris ossis occipitalis of content volume 10L was equipped with the powder trachea for this slurry, it 5.6L Taught the reaction container which the agitator, the slurry supply means, and the incubation device attached, temperature was kept at 30 degrees C, and the choke damp was blown into the bottom of churning by part for 5L/. While blowing this gas, dropping supply of the colloidal silica solution (concentration 12.5g-SiO₂/L) 1.4L was continuously carried out over 2 hours. It checked that ended an entrainment 2 hours after, carried out XRD analysis of the product, and basic zinc carbonate was generating.

[0048] (2) After putting this slurry for 2 hours, supernatant liquor was thrown away and the basic zinc carbonate slurry of 20% of slurry concentration was obtained. It checked that supernatant liquor was analyzed and the amount of silica was not. That is, it was checked that parts for all the supplied silica had been introduced into basic zinc carbonate. Feed of this slurry was carried out to the spray dryer adjusted to the inlet gas temperature of 250 degrees C, and the outlet gas temperature of 130 degrees C, and the basic zinc carbonate particle was obtained. The particle diameter of this particle was about 100 micrometers.

[0049] (3) It inserted in the core box furnace which heated this particle at 250 degrees C, and decomposed thermally for 5 hours, and the zinc-oxide very fine particle was obtained.

[0050] The specific surface area of the obtained zinc oxide was measured with the BET adsorption method, and the value of 50m²/g was acquired. The particle diameter calculated from this specific surface area is 0.02 micrometers. Moreover, it checked that analyzed a part for the silica in a zinc oxide, and a part for 4.8% of silica was included. JIS The bulk density measured based on K5101 was 0.20g/ml.

[0051] Next, in order to evaluate the dispersibility of this obtained zinc-oxide very fine particle, the above-mentioned dispersibility assessment trial was performed and permeability was measured. A result is shown in a table 1. It turns out that the zinc oxide of this invention excels [ability / light permeability and / ultraviolet-rays electric shielding] in dispersibility highly so that clearly from a table.

[0052] (Example 1 of a comparison)

(1) The zinc-oxide slurry of 50 g/L was prepared using the JIS K1401 one-sort zinc oxide and ion exchange water which were obtained with the French method. This slurry was 7L Taught to the reaction container which equipped the agitator and pars basilaris ossis occipitalis of content volume 10L with the powder trachea, and the choke damp was blown by part for bottom of churning 5L/. It checked that carried out XRD analysis of the entrainment 2 hours after, and basic zinc carbonate was generating the stop and the product.

[0053] (2) After putting this slurry for 2 hours, except for supernatant liquor, the basic zinc carbonate slurry of 20% of slurry concentration was obtained. Feed of this slurry was carried out to the spray dryer adjusted to the inlet gas temperature of 250 degrees C, and the outlet gas temperature of 130 degrees C, and the basic zinc carbonate particle was obtained. The particle diameter of this particle was about 110 micrometers.

[0054] (3) It inserted in the core box furnace which heated this particle at 250 degrees C, and decomposed thermally for 5 hours, and the zinc-oxide very fine particle was obtained.

[0055] The specific surface area of the obtained zinc oxide was measured with the BET adsorption method, and the value of 47m²/g was acquired. The particle diameter calculated from this specific surface area is 0.02 micrometers. The bulk density measured based on JIS K5101 was 0.30g/ml. Next, in order to measure the dispersibility of this obtained zinc-oxide very fine particle, the above-mentioned dispersibility assessment trial was performed and permeability was measured. A result is shown in the following table 1. Although the zinc oxide manufactured using the conventional approach contains neither aluminum nor the oxide of Si, and light permeability is high compared with an example 1 since bulk density is also high, ultraviolet-rays electric shielding ability is low, and it turns out that it is inferior to dispersibility so that clearly from a table.

[0056] (Example 2 of a comparison) Using the zinc oxide obtained in the example 1 of a comparison, in addition to the sodium-silicate water solution of computational complexity with which the amount of silica coats becomes 5 mass %, after agitating this solution strongly and making it a slurry regime, the hydrochloric acid was added gradually and the lowering silicon oxide was deposited to pH7. The zinc-oxide powder which filtration[after 1 evening standing]-washed this liquid, dried, and covered the front face with the silicon oxide was obtained. The dispersibility assessment trial of this zinc-oxide powder was performed, and permeability was measured. A result is shown in the following table 1. Although the light permeability of what covered only the front face of a zinc oxide with the silica is high compared with an example 1 as shown in a table, ultraviolet-rays electric shielding ability is low, and it turns out that it is inferior to dispersibility.

[0057] (Example 2)

(1) The zinc-oxide slurry of 50 g/L was prepared using the supernatant liquor and pure water which were obtained in the JIS K1410 three-sort zinc oxide obtained with the French method, and the example 1. This slurry was 5.6L Taught to the reaction container which equipped the pars basilaris ossis occipitalis of content volume 10L with the powder trachea, and the agitator, the slurry supply means, and the incubation device attached, temperature was kept at 40 degrees C, and the choke damp was blown by part for bottom of churning 10L/. Colloidal alumina while blowing this gas solution (concentration 12.5 g-aluminum₂O₃/L) 1.4L was continuously supplied over 2 hours. It checked that ended an entrainment 2 hours after, carried out XRD analysis of the product, and basic zinc carbonate was generating.

[0058] (2) After putting this slurry for 2 hours, supernatant liquor was thrown away and the basic zinc carbonate slurry of 27% of slurry concentration was obtained. Feed of this slurry was carried out to the spray dryer adjusted to the inlet gas temperature of 250 degrees C, and the outlet gas temperature of 130 degrees C, and the basic zinc carbonate particle was obtained. The particle diameter of this particle was about 400 micrometers.

[0059] (3) It inserted in the retort furnace (the retort was rotated by 10rpm) which heated the particle concerned at 300 degrees C, and decomposed thermally for 5 hours, and the zinc-oxide very fine particle was obtained. The specific surface area of the obtained zinc oxide was measured with the BET adsorption method, and the value of 43m²/g was acquired. The particle diameter calculated from this specific surface area is 0.02 micrometers. Moreover, it checked that analyzed a part for the alumina in a zinc oxide, and 0.9% of alumina was included. JIS The bulk density measured based on K5105 was 0.3g/ml.

[0060] Next, in order to evaluate the dispersibility of this obtained zinc-oxide very fine particle, the above-mentioned dispersibility assessment trial was performed and permeability was measured. A result is shown in the following table 1. It turns out that the zinc oxide of this invention excels [ability / light permeability and / ultraviolet-rays electric shielding] in dispersibility highly so that clearly from a table.

[0061] (Example 3)

(1) The zinc-oxide slurry of 62.5 g/L was prepared using the JIS K1410 one-sort zinc oxide and ion exchange water which were obtained with the French method. This slurry was 5.6L Taught to the reaction container which equipped the pars basilaris ossis occipitalis of content volume 10L with the powder trachea, and the agitator, the slurry supply means, and the incubation device attached, temperature was kept at 30 degrees C, and the choke damp was blown by part for bottom of churning 5L/. While blowing this gas, colloidal silica solution (concentration 25g-SiO₂/L) 1.4L was continuously supplied over 2 hours. It checked that ended an entrainment 2 hours after, carried out XRD analysis of the product, and basic zinc carbonate was generating.

[0062] (2) After putting this slurry for 2 hours, supernatant liquor was thrown away and the basic zinc carbonate slurry of 20% of slurry concentration was obtained. It checked that supernatant liquor was analyzed and the amount of silica was not. Feed of this slurry was carried out to the spray dryer adjusted to the inlet gas temperature of 250 degrees C, and the outlet gas temperature of 130 degrees C, and the basic zinc carbonate particle was obtained. The particle diameter of this particle was about 100 micrometers.

[0063] (3) It inserted in the core box furnace which heated this particle at 250 degrees C, and decomposed thermally for 5 hours, and the zinc-oxide very fine particle was obtained. The specific surface area of the obtained zinc oxide was measured with the BET adsorption method, and the value of 55m²/g was acquired. The particle diameter calculated from this specific surface area is 0.02 micrometers. Moreover, it checked that analyzed a part for the silica in a zinc oxide, and a part for 9% of silica was included. JIS The bulk density measured based on K5105 was 0.20g/ml.

[0064] Next, in order to measure the dispersibility of this obtained zinc-oxide very fine particle, the above-mentioned dispersibility assessment trial was performed and permeability was measured. A result is shown in the following table 1. It turns out that the zinc oxide of this invention excels [ability / light permeability and / ultraviolet-rays electric shielding] in dispersibility highly so that clearly from a table.

[0065]

[A table 1]

	透過率 (%)	
	550nm	350nm
実施例 1	96.65	26.32
実施例 2	96.92	28.35
実施例 3	97.65	31.63
比較例 1	95.31	34.40
比較例 2	96.46	41.56

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(54) 【発明の名称】 紫外線遮蔽用酸化亜鉛微粒子

(57) 【要約】

【課題】 分散性にすぐれ、かつ紫外線遮蔽性に優れた酸化亜鉛微粒子を提供する。

【解決手段】 比表面積から計算された平均1次粒子径が0.03 μm以下であり、粒子内部にも、AlあるいはSiの酸化物若しくは水酸化物の1種ないしは2種以上を、酸化亜鉛に対し質量比で0.1~20%含み、かつ、嵩密度が0.25 g/ml以下である分散性に優れた紫外線遮蔽用酸化亜鉛微粒子を使用する。

【特許請求の範囲】

【請求項1】 比表面積から計算された平均1次粒子径が $0.03\mu\text{m}$ 以下である酸化亜鉛微粒子であって、当該粒子内部にも、AlあるいはSiの酸化物若しくは水酸化物の1種ないしは2種以上を、酸化亜鉛に対し質量比で $0.1\sim 20\%$ 含み、かつ、嵩密度が $0.25\text{g}/\text{ml}$ 以下であることを特徴とする実質的に酸化亜鉛からなる、分散性に優れた紫外線遮蔽用酸化亜鉛微粒子。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、分散性に優れた紫外線遮蔽用酸化亜鉛微粒子に係り、詳しくは分散性が顕著に向上した酸化亜鉛微粒子に関する。

【0002】

【従来の技術】酸化亜鉛は、従来より紫外線を遮蔽する材料として知られていたが、近年オゾンホール拡大やオゾン層破壊に伴う紫外線トラブルという環境問題がメデア等で大きくとりあげられるようになり、また紫外線が人体に及ぼす予想以上の悪影響が明らかになるとともに、人体を有害な紫外線から保護するための最も代表的な材料の一つとして期待され、精力的に研究が行われ、かつ、広範囲の用途に用いられるようになってきている。そして、このような人体（皮膚）への悪影響に対処するためのものとして、紫外線遮蔽剤として酸化亜鉛を配合した日焼け止め化粧品が注目されている。

【0003】このように、近年、酸化亜鉛粒子を化粧品に配合する用途が増加するにつれて、有害な紫外線の遮蔽機能が優れていることはもちろん、同時に、配合された粒子が女性の肌を覆う創美製品である化粧品本来の自然な化粧仕上りの作用を妨害しないため、可視光線に対しては、出来るだけ透明な材料であることが強く望まれるようになった。従って、そのために、酸化亜鉛をより微細粒子化し、可視光線に対しては、実質的に透明にすることが必須となっている。

【0004】しかして、無機系化合物である酸化亜鉛系紫外線遮蔽剤は、近紫外線をも吸収・散乱することから、近紫外線を含む広い領域に渡って紫外線を遮蔽するという長所があり、また酸化亜鉛は、無機化合物であるので皮膚にアレルギーを引き起こしにくく、化粧品中に多量に配合することが可能となる。従って、特に日焼け止め化粧品に配合されて最大限に効果を発揮するものである。

【0005】そして酸化亜鉛は、その粒子径を $0.03\mu\text{m}$ 以下の超微粒子に調整すれば、可視光線の波長よりずっと小さくなるので、理論的には可視光線はほとんど吸収されず、従って化粧品の透明感を阻害することは全くないことになる。

【0006】このように微細粒子化された酸化亜鉛は、紫外線遮蔽領域の広さ、透明感、皮膚に対する安全性、紫外線遮蔽効果の持続性などの点で、従来の紫外線遮蔽材

料、すなわち有機紫外線吸収剤や酸化チタンに比べて、より優れた特徴を有するものであるといつてよい。

【0007】

【発明が解決しようとする課題】しかしながら、このよう優れた特徴を有する微粒子状酸化亜鉛にあっても、これを紫外線遮蔽剤として用いた場合には、以下に述べる問題点があることを本発明者らは見いだした。

【0008】すなわち、酸化亜鉛粒子はもともと凝集力が強いものであるが、上記のように微粒子化した場合は、その比表面積が大きいことから、その凝集力も極めて大きなものとなっている。そして、このような酸化亜鉛微粒子を化粧品等に配合する場合には、通常他の有機系の基剤と混合して用いるところ、上述したように、酸化亜鉛微粒子は凝集力が強くそれ自身で凝集してしまうため、その粒子は、当該有機系基剤中に十分に分散しない。すなわち、このように凝集した酸化亜鉛粒子は、化粧品本来の透明性を阻害するおそれがあった。

【0009】また、このような微粒子状酸化亜鉛を化粧品に配合した場合、これらが強く凝集しているため化粧品の本来有する微妙な滑らかさを低下させ、感触（肌触り）の悪化を招くという大きな問題があった。

【0010】本発明は上記問題点を解決するためになされたもので、その目的とするところは、良好な透明性を有し、紫外線遮蔽効果が高く、しかも保存性がよく十分な滑らかさを有する化粧品等を得るのに適した酸化亜鉛を提供することにある。

【0011】

【課題を解決するための手段】すなわち、本発明に従えば、比表面積から計算された平均1次粒子径が $0.03\mu\text{m}$ 以下である酸化亜鉛微粒子であって、当該粒子内部にも、AlあるいはSiの酸化物若しくは水酸化物の1種ないしは2種以上を、酸化亜鉛に対し質量比で $0.1\sim 20\%$ 含み、かつ、嵩密度が $0.25\text{g}/\text{ml}$ 以下であることを特徴とする実質的に酸化亜鉛からなる、分散性に優れた紫外線遮蔽用酸化亜鉛微粒子が提供される。

【0012】

【発明の実施の形態】以下、本発明について詳細に説明する。本発明の酸化亜鉛微粒子は、比表面積から計算された平均1次粒子径が $0.03\mu\text{m}$ 以下に微粒子化されているものである。

【0013】ここで比表面積から計算された平均1次粒子径とは、所謂BET法により比表面積を測定し、得られた値を次式（1）により計算して得られた値である。

$$d = 1.06 / S \quad (1)$$

〔式中d：平均1次粒子径（単位 μm ）、S：比表面積（単位 m^2/g ）〕

【0014】酸化亜鉛粒子の平均1次粒子径が $0.03\mu\text{m}$ を越えた場合は、基本的に可視光線の透明性が阻害され好ましくない。

【0015】本発明における酸化亜鉛粒子は、このように微細粒子化されているとともに、当該粒子内部に、更にA1あるいはSiの酸化物若しくは水酸化物の内、1種ないしは2種を、酸化亜鉛に対し質量比で0.1～20%有していることを特徴とする。

【0016】本発明におけるA1やSiの酸化物又は水酸化物（以下、A1の酸化物等と称することがある。）は、酸化亜鉛粒子の分散性を向上させる機能を有するものである。しかして、これらA1の酸化物等は、酸化亜鉛粒子の表面だけではなく粒子内部にも導入されていることが重要であり、単に粒子表面に被着又は被覆されているだけでは不十分である。その理由は、(i)酸化亜鉛を使用するに当たっては攪拌機やニーダー等によりシア（剪断力）を印加して媒体に分散させるが、当該分散作業においては、必然的に粒子にかなり強いシアが掛かるので、単に粒子表面を被覆しているだけのA1の酸化物等は、容易に粒子から剥離してしまうからである。(ii)また、シアが掛かったときに凝集粒子や融着粒子が割れる等により、新たな表面が露出し、この新たな粒子表面は、活性が高く、またA1の酸化物等が存在しないので、分散後に容易に再凝集を起こすことになる。以上のごとく、分散前の酸化亜鉛粒子表面だけをA1の酸化物等で被覆したものでは、その分散効果が十分に発揮できないのである。

【0017】本発明においては、これに対し、A1の酸化物等の分散性向上物質は、酸化亜鉛粒子内部にも導入されているので、上記のような剥離の問題もなく、また粒子が割れた場合にも、新たな露出面にA1の酸化物等が存在し再凝集も防止され、常に安定的に分散したものが得られるのである。

【0018】本発明においては、A1等は、酸化物若しくは水酸化物の形態でその1種又は2種以上が含有されるが、その含有量は、A1又はSiの酸化物又は水酸化物として酸化亜鉛に対し質量比で0.1～20%、好ましくは0.1～10%である。A1の酸化物等の含有量があまり少なく0.1%未満では、その分散性向上効果が十分に得られず、また添加量があまり過大で20%を越えて添加しても、その効果がさらに大きくなることはなく、逆に酸化亜鉛の有効量が少なくなるため酸化亜鉛本来の紫外線遮蔽効果が低下することになり好ましくない。なお、この含有量は、A1とSiを併用する場合は、その合計量として計算した値である。

【0019】本発明の酸化亜鉛微粒子は、また、嵩密度が0.25g/ml以下である。ここで嵩密度は、JISK5101に基づき測定された値であるが、この値が0.25g/ml以下と、きわめて低い値であることは、酸化亜鉛の真密度（5.6）を考慮すると、その空間占有率がわずか4.4%以下と非常に小さいことを意味する。すなわち、本発明の酸化亜鉛微細粒子は、ミクロのレベルで考察すると、空間を極めて疎な状態で占拠

していることを意味し、いわば空間中にバラバラの状態で存在していると言えるのである。このため、本発明の酸化亜鉛粒子は、きわめて分散し易い状態であることにより特徴づけられるのである。

【0020】更に本発明の粒子は、実質的に酸化亜鉛であることにより特定される。実質的に酸化亜鉛であるとは、その粉末のX線回折による主たるピークが、酸化亜鉛のものであればよいことを示し、酸化亜鉛の他に、合成時に混入した不純物、原料に含まれる不純物等を含んでいてもよい。

【0021】本発明の酸化亜鉛微粒子は、その分散性が極めて優れたものであるが、分散性の評価方法としては、次に示す測定方法が用いられる。

【0022】1. 試料の酸化亜鉛1.5gを精秤し、10%PVA/0.2%ヘキサメタリン酸ナトリウム溶液50gに加え、ホモジナイザー（日本精機製作所社製、エースホモジナイザーAM-7型）で10分（×1500rpm）分散し、酸化亜鉛粒子の分散液を得る。

【0023】2. オートアプリアケーター（井元製作所社製）上に50μmのアプリアケーターをセットし、PETフィルム（厚さ100μm）をセットする。適量の上記酸化亜鉛粒子の分散液を、当該PETフィルム上にのせ、オートアプリアケーターのスイッチを入れ塗布を開始する。送り速度は、目盛20に設定する。かくしてフィルムの端まで分散液を塗布したら、スイッチを切る。

【0024】3. 塗膜を1日乾燥させた後、その厚さをマイクロメーターで測定する。膜の厚さ（約5～10μm）が揃っていて、一定な部分を切り出し、分光器（日本分光社製、V-570ST型）内の積分球の入射光が入る部分に試験片を貼り付け、透過率を測定する。

【0025】以上のごとくして測定された透過率においては、可視光透過率が高く、紫外光透過率が低いものほど酸化亜鉛粒子が細かく分散されていることを示す。

【0026】本発明の酸化亜鉛微粒子は、上記のごとくして評価される粒子の分散性がきわめて良好である。この分散性向上のメカニズムは、現在のところ完全には明確ではないが、本発明者らは、一応以下のものであろうと推察している。すなわち、酸化亜鉛粒子にA1あるいはSiの酸化物若しくは水酸化物が含まれることにより、当該粒子表面が不活性となり、粒子同士の凝集性が減少するとともに、媒体との親和性が向上するためではないかと推察している。

【0027】本発明に係わる酸化亜鉛の製造方法としては、特に限定するものではないが、例えば以下の方法が採用される。すなわち、酸化亜鉛を含む水スラリーに二酸化炭素ガスを吹込み、塩基性炭酸亜鉛を合成する際に、水分散性のアルミニウム水酸化物、アルミニウム酸化物若しくは水分散性のケイ素水酸化物、ケイ素酸化物を添加し、得られた当該塩基性炭酸亜鉛スラリーを、流動層乾燥、媒体流動層乾燥、気流乾燥及又は噴霧乾燥し

た後、加熱分解することにより酸化亜鉛を製造する方法が好ましい。

【0028】原料として用いられる酸化亜鉛としては、所謂酸化亜鉛であればどのようなものであってもよく、例えば、亜鉛を溶融・蒸発させ気相で酸化するフランス法、亜鉛鉱石を仮焼・コークス還元・酸化するアメリカ法、亜鉛塩溶液にソーダ灰を加えて塩基性炭酸亜鉛を沈殿させ、乾燥・焼成する湿式法（加熱分解法）等のいずれで製造したものでよいが、高純度の酸化亜鉛微粒子を得るためには、純度の高い酸化亜鉛を用いることが好ましい。

【0029】この原料酸化亜鉛を懸濁させてスラリーとする水としては、特に限定するものではなく、製品である酸化亜鉛の要求純度に応じて鉄錆等の不純物粒子を除いた上水道水、イオン交換した純水、又は蒸留水の何れを用いてもかまわない。また、導入する二酸化炭素ガスは、純粋なガスとしてそのまま使用してもよいが、場合によっては、空気や窒素等の希釈ガスにより適当な濃度に希釈して使用することも可能である。

【0030】塩基性炭酸亜鉛生成反応を行うための装置としては、特に限定するものではないが、例えば攪拌手段、加熱手段、ガス導入・分散手段、及びA1の酸化物等の導入手段を備え、酸化亜鉛粒子を沈殿させることなく浮遊させてスラリー状態に保持し、この中へ二酸化炭素ガス及びA1の酸化物等を導入して、A1の酸化物等の粒子の存在下に酸化亜鉛粒子と二酸化炭素ガスと充分接触せしめて反応を遂行する形式の攪拌槽型の反応装置が好ましい。

【0031】原料酸化亜鉛のスラリー濃度としては、少なくとも0.1～20質量%、好ましくは0.1～10質量%、より好ましくは1～5質量%の比較的薄い濃度とすることが望ましい。スラリー濃度がこの範囲を超える場合は、大粒径の塩基性炭酸亜鉛が生成したり、凝集粒子が生成しやすくなり、本発明で目的とする分散性の良い微粒子とすることが困難になる。一方スラリー濃度がこれよりあまり薄い場合は、以後の乾燥工程等において除去すべき水の量が過大となり製造効率が低下しエネルギー的にも好ましくない。

【0032】二酸化炭素ガスの導入方法としては、スラリーとガスが効果的に接触しうるものであればいかなる方法も用いられ、特に限定するものではないが、例えば反応槽底部に多孔板や散気管のごときガス分散器（スパーージャ）を設置し、このスパーージャを通じて二酸化炭素ガスを液中に吹き込み、さらに好ましくは攪拌羽根によりこれを細分化し、二酸化炭素ガスを微小気泡群としてスラリー中全体に、分散化して導入する方法；反応槽として密閉容器を使用し、加圧した二酸化炭素ガスを導入し、スラリー上部の自由表面からガスを吸収させる方法等の手段が採用できる。後者の場合は、攪拌によりボルテックスを形成し、当該スラリー液面の表面更新を強制

的に行いガス吸収を促進することがより好ましい。

【0033】二酸化炭素を吹き込んで塩基性炭酸亜鉛を生成させる際に、A1又はSiの酸化物若しくは水酸化物の内、1種ないしは2種を、当該酸化亜鉛に対し質量比で0.1～20%、好ましくは0.1～10%有するように、当該酸化物若しくは水酸化物の原料を添加し塩基性炭酸亜鉛中に含有させる。原料として特に好ましい例としては、コロイダルシリカ、コロイダルアルミナ等の微細粒子ゾルが挙げられ、これらを、滴下装置のごとき導入手段により反応液中に導入する。なお、その他、二酸化炭素ガスを吹込む事によりA1、Siの酸化物若しくは水酸化物を生じるものであればいかなる化合物を用いても良い。これらのコロイダルシリカ等は、二酸化炭素ガスの供給速度に合わせて、滴下等の手段でほぼ連続的に導入することが好ましい。かくして、塩基性炭酸亜鉛の粒子が生成・成長する近傍には、A1の酸化物等の微細ゾル粒子が常に存在するので、当該粒子成長は、A1の酸化物等の微細粒子を取り込むように行われ、かくして形成される塩基性炭酸亜鉛粒子内部にはA1の酸化物等が存在することになると考えられる。

【0034】攪拌手段としては、通常の攪拌機、例えば櫓型攪拌機、プロペラ型攪拌機、タービン型攪拌機等のいずれもが好適に使用される。

【0035】本発明の塩基性炭酸亜鉛生成反応は、実際には種々の方式によって実施することができるが、例えば、反応槽にまず酸化亜鉛スラリーを仕込んでおき、これに二酸化炭素ガスを連続的に供給して塩基性炭酸亜鉛スラリーを生成させる半連続法（半回分法）；酸化亜鉛スラリーと二酸化炭素ガスの両者を連続的に反応槽に供給して塩基性炭酸亜鉛スラリーを生成させ、当該生成した塩基性炭酸亜鉛スラリーを連続的に反応槽から溢流させる等して抜き出す連続法等の方法が好ましく採用される。

【0036】塩基性炭酸亜鉛生成反応の反応温度としては、特に限定するものではないが、10～80℃、好ましくは20～60℃である。反応自体は、温度が高い程高速で進行するが、二酸化炭素ガスの水に対する溶解度は、温度が高くなると減少し、液中のガス濃度は低下する。従って、反応温度は、上記した温度範囲より低くても、高くても、総括的な反応速度が遅くなり好ましくない。また、反応時間（連続法の場合は、反応槽における平均滞留時間）は、反応温度、導入される二酸化炭素濃度等により変わりうるが、通常10分～10時間、好ましくは30分～5時間程度である。なお、温度保持のため、反応器は、加熱手段や保温手段及び温度制御手段を備えることも好ましい。

【0037】本発明においては、以上の塩基性炭酸亜鉛生成反応により得られた塩基性炭酸亜鉛を含むスラリーを流動層乾燥、媒体流動層乾燥、気流乾燥及又は噴霧乾燥等により乾燥し、水分を除去して乾燥粉末とする。

【0038】この場合、塩基性炭酸亜鉛を含むスラリーのスラリー濃度は、かなり低いので、これをそのまま乾燥するのは熱エネルギー経済上望ましくない。従って、好ましくは、予め当該スラリーを濃縮、特に機械的手段により濃縮することが望ましい。

【0039】スラリーの濃縮度については、当該濃縮スラリーが流動性を保持し、流動層乾燥器等に微粒化して供給・処理される範囲であれば特に制限はないが、一般的にはスラリー濃度として20～50質量%、好ましくは20～45質量%、さらに好ましくは25～40質量%の範囲であることが取扱い上及び経済性の点から望ましい。

【0040】濃縮のための機械的手段としては、特に限定するものではないが、シックナー等を用いる沈殿濃縮、遠心沈降機を用いる遠心沈降、液体サイクロンを用いる遠心分級等が好ましく使用され、所望の濃縮度や処理量等に応じて最適な装置を採用することができる。

【0041】本発明においては、塩基性炭酸亜鉛スラリーは、以上のごとく、好ましくは予め濃縮され、流動層乾燥器、媒体流動層乾燥器、气流乾燥器及又は噴霧乾燥器等のごとき乾燥装置に供給され乾燥される。供給されたスラリーは、かかる乾燥装置内で、微細粒子を含む液滴となり、これが乾燥用の熱風により流動層を形成し、浮遊しながら乾燥されるか（流動層乾燥、媒体流動層乾燥）、又は熱風により搬送されながら極めて短時間で乾燥され（气流乾燥及又は噴霧乾燥）、塩基性炭酸亜鉛の乾燥粉末が得られる。

【0042】乾燥装置としては、最も分散された塩基性炭酸亜鉛の乾燥微粒子が得られる点で噴霧乾燥器が特に好ましい。噴霧乾燥器を使用する場合の噴霧機としては、回転円板、二流体ノズル、加圧ノズル等が適宜採用でき、また乾燥用熱風温度は、入口で200～300℃、出口で100～150℃程度にすることが好ましい。

【0043】最後に当該乾燥された塩基性炭酸亜鉛を加熱分解（焼成）し酸化亜鉛とする。加熱分解温度は、塩基性炭酸亜鉛を分散性の良い微粒子状の酸化亜鉛に分解する温度で、200～1000℃、好ましくは200～500℃、さらに好ましくは250～350℃の温度が望ましい。これよりあまり温度が低いと分解が不十分になり、またこれよりあまり温度が高すぎると凝集や焼結により粒子が成長しすぎることとなり、何れも分散性が悪くなるため好ましくない。加熱分解時間は、処理量、加熱温度、加熱炉の型等によっても異なりうるが通常30分～20時間、好ましくは1～10時間程度である。

【0044】加熱分解は、空気等の酸化性雰囲気下で、塩基性炭酸亜鉛粒子を上記温度に加熱しうる炉により行われる。加熱炉としては、特に限定するものではなく、例えば箱形炉、回転炉（ロータリーキルン）、移動層炉、流動層炉、電気炉、ガス加熱炉、赤外線加熱炉等が

好適に用いられる。

【0045】加熱分解後の酸化亜鉛粒微粒子は、分散性に優れており、そのまま本発明の化粧品等の紫外線遮蔽用に使用することができる。なお、所望により、ボールミル、ロッドミル、アトリションミル、ジェットミル、ミクロンミル等の微粉碎機により更に粉碎処理してから使用することもできる。これらの微粉碎機は、配合する化粧品等や塗料などに応じて適宜選択される。

【0046】

【実施例】以下、実施例により本発明を説明する。ただし、これらは単なる実施の態様の一例であり、本発明の技術的範囲がこれらによりなんら限定されるものではない。

【0047】（実施例1）

（1）フランス法によって得たJIS K1410 1種酸化亜鉛と、イオン交換水を用いて62.5g/Lの酸化亜鉛スラリーを調製した。このスラリーを、内容積10Lの、底部に散気管を装備し、攪拌機、スラリー供給手段及び保温機構のついた反応容器に5.6L仕込み、温度を30℃に保ち攪拌下に、5L/分で二酸化炭素ガスを吹込んだ。このガスを吹込む間コロイダルシリカ溶液（濃度12.5g-SiO₂/L）1.4Lを2時間かけて連続して滴下供給した。2時間後に吹き込みを終了し、生成物をXRD分析して塩基性炭酸亜鉛が生成していることを確認した。

【0048】（2）このスラリーを2時間静置した後、上澄液を捨て、スラリー濃度20%の塩基性炭酸亜鉛スラリーを得た。上澄液を分析してシリカ分のないことを確認した。すなわち供給したシリカ分は、すべて塩基性炭酸亜鉛中に導入されたことが確認された。このスラリーを入口ガス温度250℃、出口ガス温度130℃に調整されたスプレードライヤーにフィードし、塩基性炭酸亜鉛粒子を得た。この粒子の粒子径は約100μmであった。

【0049】（3）この粒子を250℃に加熱した箱型炉に装入し5時間加熱分解し、酸化亜鉛微細粒子を得た。

【0050】得られた酸化亜鉛の比表面積をBET法によって測定し、50m²/gの値を得た。この比表面積から計算される粒子径は0.02μmである。また、酸化亜鉛中のシリカ分を分析し4.8%のシリカ分を含むことを確認した。JIS K5101に基づいて測定した嵩密度は、0.20g/mlであった。

【0051】次にこの得られた酸化亜鉛微細粒子の分散性を評価するために、上述の分散性評価試験を行ない、透過率を測定した。結果を表1に示す。表から明らかに、本発明の酸化亜鉛は、可視光透過率、紫外線遮蔽能が高く分散性に優れていることが分かる。

【0052】（比較例1）

（1）フランス法によって得たJIS K1401 1種

酸化亜鉛、イオン交換水を用いて50 g/Lの酸化亜鉛スラリーを準備した。このスラリーを、内容積10 Lの攪拌機と底部に散気管を装備した反応容器に7 L仕込み、攪拌下5 L/分で二酸化炭素ガスを吹込んだ。2時間後に吹き込みを止め、生成物をXRD分析して塩基性炭酸亜鉛が生成していることを確認した。

【0053】(2) このスラリーを2時間静置した後、上澄液を除き、スラリー濃度20%の塩基性炭酸亜鉛スラリーを得た。このスラリーを入口ガス温度250℃、出口ガス温度130℃に調整されたスプレードライヤーにフィードし、塩基性炭酸亜鉛粒子を得た。この粒子の粒子径は、約110 μmであった。

【0054】(3) この粒子を250℃に加熱した箱型炉に装入し5時間加熱分解し、酸化亜鉛微細粒子を得た。

【0055】得られた酸化亜鉛の比表面積をBET法によって測定し47 m²/gの値を得た。この比表面積から計算される粒子径は0.02 μmである。JIS K 5101に基づいて測定した嵩密度は0.30 g/mlであった。次にこの得られた酸化亜鉛微細粒子の分散性を測定するために、上述の分散性評価試験を行ない透過率を測定した。結果を下表1に示す。表から明らかなように、従来の方法を用いて製造した酸化亜鉛は、AlやSiの酸化物等を含有せず、また嵩密度も高いため実施例1に比べ可視光透過率は高いが、紫外線遮蔽能が低く、分散性に劣ることが分かる。

【0056】(比較例2) 比較例1で得られた酸化亜鉛を用い、シリカ被覆量が5質量%となる計算量のケイ酸ナトリウム水溶液に加え、この溶液を強く攪拌してスラリー状態にした後塩酸を徐々に加えてpH7まで下げケイ素酸化物を析出させた。この液を1晩静置後濾過洗浄、乾燥して表面をケイ素酸化物で被覆した酸化亜鉛粉末を得た。この酸化亜鉛粉末の分散性評価試験を行い、透過率を測定した。結果を下表1に示す。表から分かるように酸化亜鉛の表面のみをシリカで被覆したものは、実施例1に比べ可視光透過率は高いが、紫外線遮蔽能が低く、分散性に劣ることが分かる。

【0057】(実施例2)

(1) フランス法によって得たJIS K 1410 3種酸化亜鉛、実施例1で得られた上澄液及び純水を用いて50 g/Lの酸化亜鉛スラリーを調製した。このスラリーを内容積10 Lの、底部に散気管を装備し、攪拌機、スラリー供給手段及び保温機構のついた反応容器に5.6 L仕込み、温度を40℃に保ち攪拌下10 L/分で二酸化炭素ガスを吹込んだ。このガスを吹込む間コロイダルアルミナ溶液(濃度12.5 g-Al₂O₃/L) 1.4 Lを2時間かけて連続して供給した。2時間後に吹き込みを終了し生成物をXRD分析して塩基性炭酸亜鉛が生成している事を確認した。

【0058】(2) このスラリーを2時間静置した後、

上澄液を捨て、スラリー濃度27%の塩基性炭酸亜鉛スラリーを得た。このスラリーを入口ガス温度250℃、出口ガス温度130℃に調整されたスプレードライヤーにフィードし、塩基性炭酸亜鉛粒子を得た。この粒子の粒子径は約400 μmであった。

【0059】(3) 当該粒子を300℃に加熱したレトルト炉(レトルトは10 rpmで回転させた)に装入し5時間加熱分解し、酸化亜鉛微細粒子を得た。得られた酸化亜鉛の比表面積をBET法によって測定し43 m²/gの値を得た。この比表面積から計算される粒子径は0.02 μmである。また、酸化亜鉛中のアルミナ分を分析し0.9%のアルミナを含むことを確認した。JIS K 5105に基づいて測定した嵩密度は0.3 g/mlであった。

【0060】次にこの得られた酸化亜鉛微細粒子の分散性を評価するために上述の分散性評価試験を行ない透過率を測定した。結果を下表1に示す。表から明らかなように本発明の酸化亜鉛は、可視光透過率、紫外線遮蔽能が高く分散性に優れていることが分かる。

【0061】(実施例3)

(1) フランス法によって得たJIS K 1410 1種酸化亜鉛、イオン交換水を用いて62.5 g/Lの酸化亜鉛スラリーを調製した。このスラリーを内容積10 Lの底部に散気管を装備し、攪拌機、スラリー供給手段及び保温機構のついた反応容器に5.6 L仕込み、温度を30℃に保ち攪拌下5 L/分で二酸化炭素ガスを吹込んだ。このガスを吹込む間コロイダルシリカ溶液(濃度25 g-SiO₂/L) 1.4 Lを2時間かけて連続して供給した。2時間後に吹き込みを終了し生成物をXRD分析して塩基性炭酸亜鉛が生成していることを確認した。

【0062】(2) このスラリーを2時間静置した後、上澄液を捨て、スラリー濃度20%の塩基性炭酸亜鉛スラリーを得た。上澄液を分析してシリカ分のないことを確認した。このスラリーを入口ガス温度250℃、出口ガス温度130℃に調整されたスプレードライヤーにフィードし、塩基性炭酸亜鉛粒子を得た。この粒子の粒子径は約100 μmであった。

【0063】(3) この粒子を250℃に加熱した箱型炉に装入し5時間加熱分解し、酸化亜鉛微細粒子を得た。得られた酸化亜鉛の比表面積をBET法によって測定し55 m²/gの値を得た。この比表面積から計算される粒子径は0.02 μmである。また、酸化亜鉛中のシリカ分を分析し9%のシリカ分を含むことを確認した。JIS K 5105に基づいて測定した嵩密度は0.20 g/mlであった。

【0064】次にこの得られた酸化亜鉛微細粒子の分散性を測るために上述の分散性評価試験を行ない透過率を測定した。結果を下表1に示す。表から明らかなように本発明の酸化亜鉛は、可視光透過率、紫外線遮蔽能が高く分散性に優れていることがわかる。

【0065】

【表1】

	透過率 (%)	
	550nm	350nm
実施例1	96.65	26.32
実施例2	96.92	28.35
実施例3	97.65	31.63
比較例1	95.31	34.40
比較例2	96.46	41.56

【0066】

【発明の効果】表から明らかなように本発明の酸化亜鉛微粒子は、可視光透過率、紫外線遮蔽能が高く分散性に優れており、分散性に優れた紫外線遮蔽用の酸化亜鉛微

粒子であることがわかる。従って化粧品や塗料などの紫外線遮蔽と同時に透明性が必要な各種用途に好適に用いられる。

フロントページの続き

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